

## 裂冠牛奶菜中一新奇C<sub>21</sub>甾体甙\*

### A NOVEL C<sub>21</sub> STEROIDAL GLYCOSIDE FROM MARS DENIA INCISA\*

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Besides a series of normal C<sub>21</sub>steroids from *Marsdenia incisa* incisa P.T.Li et Y.P.Li, a small amount of novel C<sub>21</sub> steroidal glycoside (I) had been isolated. The mild acidic hydrolysis of (I) afforded genin-(I). By spectroscopic analyses of IR, EIMS, FDMS, <sup>1</sup>H NMR, <sup>13</sup>C NMR (DEPT, PRFT), <sup>1</sup>H-<sup>1</sup>H COSY, <sup>1</sup>H-<sup>13</sup>C COSY for (I) and (I), (I) had been deduced as B-nor (7)-6 $\beta$ -formyl-pregnane-3 $\beta$ , 5 $\beta$ , 8 $\beta$ , 12 $\beta$ , 14 $\beta$ , 17 $\beta$ , 20-heptatol, named neomarinogenin, (I) had been deduced as neomarinogenin 3-O- $\beta$ -D-thevetopyranosyl- (1 $\rightarrow$ 4)- $\beta$ -D-cymaropyranosyl- (1 $\rightarrow$ 4)- $\beta$ -D-cymaropyranoside, named neomarinoside. Their physical and spectral data were as follows.

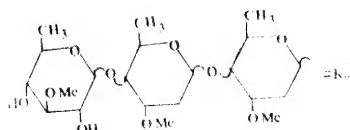
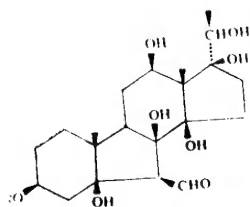
Neomarinogenin (I). A colorless prism from Me<sub>2</sub>CO, mp 202—205°C,  $[\alpha]_D^{25} + 28.81^\circ$  (MeOH, c 0.05), C<sub>21</sub>H<sub>34</sub>O<sub>8</sub> (Found: C, 60.76; H, 8.19, C<sub>21</sub>H<sub>34</sub>O<sub>8</sub> requires C, 60.87. H, 8.21%), IR  $\nu_{max}^{KBr}$  cm<sup>-1</sup>: 3450 (OH), 1700 (C=O), 1050 (C-O-C), EIMS m/z: 397 (M-OH), 380 (397-OH), 379, 378 (M-2H<sub>2</sub>O), 36, (M-3H<sub>2</sub>O), 342 (M-4H<sub>2</sub>O), 333, 315, 287, 43 (base peak). <sup>1</sup>H NMR (400 MHz, pyridine-d<sub>5</sub>): 1.38 (3H, s, 19-Me), 1.60 (3H, d, J = 6.4Hz, 21-Me), 2.06 (3H, s, 18-Me), 2.58 (1H, d, J = 4.4Hz, 7-H), 4.08 (1H, m, 3-Ha), 4.48 (1H, q, J = 5.6Hz, 20-H), 4.62 (1H, dd, J = 9.6, 6.8 Hz, 12-Ha), 10.59 (1H, d, J = 4.4 Hz, 6-H), <sup>13</sup>C NMR (100.614 MHz, pyridine-d<sub>5</sub>): 34.52 (t, C-1), 29.39 (t, C-2), 64.77 (d, C-3), 40.92 (t, C-4), 85.97 (s, C-5), 205.27 (d, C-6), 64.17 (d, C-7), 85.34 (s, C-8), 47.75 (d,

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C-9), 45.79 (s, C-10), 27.96 (t, C-11), 72.68 (d, C-12), 60.02 (s, C-13), 88.92 (s, C-14), 34.52 (t, C-15), 33.35 (t, C-16), 87.43 (s, C-17), 12.17 (q, C-18), 19.58 (q, C-19), 72.68 (d, C-20), 17.88 (q, C-21)。

Neomarinoside (I), A white powder from MeOH, mp 150—155°C,  $[\alpha]_D^{25} - 2.37^\circ$  (MeOH, c 0.10),  $C_{42}H_{70}O_{18}$  (Found: C, 53.78; H, 8.31;  $C_{42}H_{70}O_{18} \cdot 4H_2O$  requires: C, 53.96; H, 8.35%), IR  $\nu_{max}^{KBr} cm^{-1}$ : 3440 (OH), 1700 (C=O), 1050—1100 (C-O-C), FDMS  $m/z$ : 885 (M+Na)<sup>+</sup>,  $^1H$  NMR (500MHz, pyridine- $d_5$ ): 1.28 (3H, s, 19-Me), 1.36 (3H, d,  $J = 6.2$  Hz, 6'''-Me), 1.49 (3H, d,  $J = 6.1$  Hz, 21-Me), 1.58 (3H, d,  $J = 6.0$  Hz, 6''-Me), 1.59 (3H, d,  $J = 6.2$  Hz 6'-Me), 2.46 (1H, d,  $J = 4.3$  Hz, 7-H), 3.45 (1H, dd,  $J = 9.6, 2.8$  Hz, 4'-H), 3.55 (3H, s, 3'-OMe), 3.56 (3H, s, 3''-OMe), 3.58 (1H, dd,  $J = 10.7, 3.3$  Hz, 4''-H), 3.61 (1H, dd,  $J = 9.9, 6.0$  Hz, 4'''-H), 3.62 (1H, dd,  $J = 8.5, 6.0$  Hz, 3'''-H), 3.73 (1H, dq,  $J = 9.3, 6.2$  Hz, 5'''-H), 3.90 (3H, s, 3'''-OMe), 3.93 (1H, m, 3-H), 3.96 (1H, dd,  $J = 9.0, 6.5$  Hz, 2'''-H), 4.03 (1H, dd,  $J = 12.8, 3.3$  Hz, 12-H<sub>A</sub>), 4.05 (2H, ddd,  $J = 3.6, 3.0, 2.7$  Hz, 3' and 3''-H), 4.16 (1H, dq,  $J = 9.4, 6.1$  Hz, 5''-H), 4.20 (1H, dq,  $J = 9.3, 6.0$  Hz, 4'-H), 4.45 (1H, q,  $J = 6.4$  Hz, 20-H), 4.76 (1H, d,  $J = 7.8$  Hz, 1'''-H), 5.09 (1H, dd,  $J = 9.6, 1.8$  Hz, 1''-H), 5.24 (1H, dd,  $J = 9.5, 1.8$  Hz, 1'-H), 10.50 (1H, d,  $J = 4.3$  Hz, 6-H;  $^{13}C$  NMR (125.759 MHz, pyridine- $d_5$ ): 34.48 (t, C-1), 26.91 (t, C-2), 72.76 (d, C-3), 37.36 (t, C-4), 85.42 (s, C-5), 205.28 (d, C-6), 85.40 (s, C-8), 46.71 (d, C-9), 45.67 (s, C-10), 27.87 (t, C-11), 72.66 (d, C-12), 60.06 (s, C-13), 89.02 (s, C-14), 33.82 (t, C-15), 33.54 (t, C-16), 87.37 (s, C-17), 12.30 (q, C-18), 19.80 (q, C-19), 72.60 (d, C-20), 17.87 (q, C-21), 97.81 (d, C-1'), 36.87 (t, C-2'), 77.89 (d, C-3'), 83.08 (d, C-4'), 69.04 (d, C-5'), 18.55 (q, C-6'), 58.74 (q, C-7'), 100.37 (d, C-1''), 37.09 (t, C-2''), 78.13 (d, C-3''), 83.27 (d, C-4''), 69.33 (C-5''), 18.55 (q, C-6''), 58.81 (q, C-7''), 106.20 (d, C-1'''), 75.08 (d, C-2'''), 87.82 (d, C-3'''), 75.87 (d, C-4'''), 72.76 (d, C-5'''), 18.53 (q, C-6'''), 60.98 (q, C-7'''). The structures of (I) and (II) were given in the following Chart The detail study in progress will be reported in another paper.



I R = H, II R = Ra